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**Final Technical Report on Artificial Corrosion of Cu-Ni Alloys
by Sulfide Minerals - A Potentially Protective Mechanism**

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Terri L. Woods*

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Greenville, NC 27858-4353

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The objectives of this investigation were to gain a clearer understanding of the nature of the corrosion products formed on Cu-Ni alloys in sulfide-polluted seawater. In particular, we wanted to identify the chemical and physical conditions under which the various copper sulfide minerals formed adherent - and potentially protective - films on these alloys. In order to do this, we immersed $\text{Cu}_{90}\text{Ni}_{10}$ coupons in artificial seawater solutions containing varying amounts of O_2 and S^{2-} . The oxygen content of the solutions was controlled by purging the artificial seawater solutions to varying degrees with N_2 gas. The sulfide levels were regulated by the addition of $\text{Na}_2\text{S } 9\text{H}_2\text{O}$. To enhance the crystallinity of the corrosion products, the seawater solutions were not stirred, nor were their compositions monitored or adjusted, during the 119-139 days of corrosion-product formation.

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Department of Geology
Graham Building

919-757-6360

Dr. Brenda Little
Code 333, Building 1105
Naval Oceanographic and Atmospheric Research Laboratory
NSTL Station, Mississippi
39529-5004

RE: Final Technical Report on Contract # N00014-90-J-6002:
Artificial Corrosion of Cu-Ni alloys by sulfide minerals - A
potentially protective mechanism

Dear Dr. Little.

Enclosed you will find three copies of the Final Technical Report for the indicated grant. Other copies of the report have been sent to the offices indicated in the distribution list. This summary is more of a status report than a final report in that the analyses of the corrosion products are not yet complete. Because Contract # N00014-90-J-6002 was later supplemented by Contract # N00014-90-J-6010, the number of methods by which the samples are to be analyzed was increased thereby requiring more time to finish all the analytical work. The enclosed report includes tables summarizing the analyses completed thus far and a preliminary synthesis of these results. Final analysis of these specimens and interpretation of the results should be completed by the end of the current calendar year. Please let me know if you need more information than I have included in the enclosed reports.

Sincerely,

Dr. Terri L. Woods

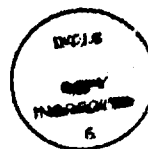
Dr. Terri L. Woods
Assistant Professor

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The objectives of this investigation were to gain a clearer understanding of the nature of the corrosion products formed on Cu-Ni alloys in sulfide-polluted seawater. In particular, we wanted to identify the chemical and physical conditions under which the various copper sulfide minerals formed adherent -- and potentially protective -- films on these alloys. In order to do this, we immersed Cu90Ni10 coupons in artificial seawater solutions containing varying amounts of O_2 and S^{2-} . The oxygen content of the solutions was controlled by purging the artificial seawater solutions to varying degrees with N_2 gas. The sulfide levels were regulated by the addition of $Na_2S \cdot 9H_2O$. To enhance the crystallinity of the corrosion products, the seawater solutions were not stirred, nor were their compositions monitored or adjusted, during the 119-139 days of corrosion-product formation.

The results presented in this report are preliminary. In fact, it represents more of a status report than a final report because the analyses of the corrosion products are not yet complete. Because this contract was later supplemented by Contract # N00014-90-J-6010, the additional analytical methods made possible by the latter contract are only in the initial stages (i.e., X-ray Photoelectron Spectroscopy (XPS) analyses to be conducted by Dr. James Castle of the University of Surrey). At this time, the chemistry of the artificial seawater solutions to which the copper coupons were

exposed has been analyzed (Table 1). Also, all corroded Cu-Ni coupons have been photographed to provide a permanent record of the macroscopic texture and color of the corrosion product, as well as its "adherence" (Table 2). The SEM and EDX work is in the final stages, but the synthesis of these results is incomplete (Tables 2 & 3).

The tables included in this report describe the results we have so far. We still have a long way to go to interpret all this information, and even to determine the best way to display it. As we proceed with our analysis we will undoubtedly discover the most significant features of the samples and solutions, and be better able to draw conclusions as to the processes occurring during the corrosion of the copper coupons. The XPS analyses from Dr. Castle, providing definitive mineralogical identification, will be indispensable in unraveling the complex history of these specimens.

The only sulfide mineral as yet identified with any certainty is chalcocite, although a phase tentatively labelled covellite has also been observed. A number of other Cu-S compounds with differing morphologies remain to be identified. The presence of the potentially protective phase djurleite ($\text{Cu}_{1.96-1.97}\text{S}$) can not be determined by SEM and EDX analyses alone, but can hopefully be determined by XPS analysis. Some of the Cu-S phases contain significant amounts of Ni, which may give us an indication of the chemical conditions under which significant de-alloying of the Cu-Ni coupons occurs. Cuprite (Cu_2O) has been identified in some of

the corrosion products along with some other non-sulfide minerals including azurite ($\text{Cu}_2(\text{OH})_2(\text{CO}_3)$) and atacamite ($\text{Cu}_2\text{Cl}(\text{OH})$). The identification of the latter two minerals will contribute to our understanding of the chemistry of the seawater solutions. Also, the presence or absence of cuprite may help us to determine the conditions which contribute to formation of an adherent - and potentially protective - sulfide film.

A few general observations can be made about the conditions under which sulfide films form. Adherent films appear to form only in solutions with less than 0.10 mg/L O_2 or with high initial sulfide levels (i.e., $\text{S}^{2-} > 200$ ppm). Solutions with a final pH less than 7.0 were also less likely to form adherent sulfide coatings. The thickest, most adherent sulfide films formed in solutions with an initial O_2 level less than 0.02 mg/L and with initial sulfide concentrations greater than 115 ppm. The sulfide minerals formed in various solutions have not been definitely identified, nor has the degree of corrosion protection afforded to the Cu-Ni coupons by the various sulfide films yet been determined.

In summary, Cu-Ni coupons have been exposed to corrosion by sulfide-rich seawater solutions for up to 139 days. The coupons have been removed from the solutions, photographed and analyzed by SEM and EDX. The pH, Eh, oxygen and sulfide concentrations of the solutions have been determined. XPS analyses of the corroded coupons remain to be done and final interpretation of the results is still in its initial stages.

Table 1. Summary of chemical data for synthetic seawater solutions. Data was taken when wafers were placed in solutions and when they were removed.

Specimen Number	Oxygen Mg/L Initial	Eh Final	Initial pH	Final pH	Initial Sulfide ppm	Final Sulfide ppm
1,2	>.10	223.9	8.14	8.18	1	BDL
3,4	>.10	216.3	8.45	8.10	8	BDL
5,6	>.10	213.6	8.14	7.49	40	BDL
7,8	>.10	229.6	8.42	7.47	115	BDL
16,17	>.10	228.3	8.15	6.70	154	BDL
10,11	>.10	150.3	8.40	8.06	192	BDL
12,13	>.10	100.3	8.35	8.24	256	BDL
14,15	>.10	82.9	8.39	7.89	289	BDL
20,21	.10	206	8.10	7.86	1	BDL
22,23	.10	204	7.84	7.58	8	BDL
24,25	.10	193	8.24	6.82	58	BDL
26,27	.10	186	8.25	6.80	115	BDL
30,31	.02	-361	8.36	8.71	154	58
32,33	.02	-357	8.07	8.65	192	96
34,35	.02	-386	8.29	8.45	248	160
36,37	.10	-35	8.42	8.41	289	BDL

Table 2: Surface examinations of wafers, including macroscopic and microscopic descriptions.

Specimen Number	Macroscopic Description	Microscopic Description
2	Thin reddish brown coating, poorly adherent.	In areas where reddish brown product washed away, a thin film containing numerous cracks was visible. Brownish red coating appeared as lepispherical shaped crystals composed of Cu and Cl.
4	Thick adherent green coating, abundant with acicular white crystals	Top coating consists of packets of acicular calcium carbonate crystals. Copper chloride, lepispherical shaped crystals were also abundant in the top layer. Bottom layer consists of a thin black film containing cracks. The thin black film is topped by cubes with an edx analysis of Cu and Cu-O rich dipyrromidal crystals.
6	Thin, poorly adherent black coating with black tarnish where black precipitate washed away	Carbonate crystals are rare but pseudo-hexagonal shape is more distinct. The black precipitate consists of irregularly shaped nodules, consisting predominantly of Cu and S, and doped with Fe, Ni and Al.
8	Thick, poorly adherent black coating, coating washed off on edges exposing tarnished wafer	Porous underlayer composed of Cu-Fe-Ni-S. Upper layer covered with Cu-S nodules. Several other constituents could be found in or on the upper layer: cubes consisting of Cu and S several of these appeared to be chewed up. There were also rounded Ni rich nodules over some of the surface.
16	Thick, non-adherent dark gray to black coating	Upper coating is predominantly pseudo-hexagonal crystal composed of Cu and S. The pseudo-hexagonal crystals were poorly formed and appeared to be growing into neighboring crystals. Cubes composed of Cu and S were abundant in regions where black product was washed off.
10	Thick, non-adherent black coating	Cubes with edx analysis of Cu were abundant. (edx is not capable of reading oxygen). Pseudo-hexagonal crystals composed of Cu and S were abundant. Intermixed with pseudo-hexagonal crystals were thin lacy products composed of Cu and S.
12	Thick, brown, adherent microcrystalline coating	Play hexagonal and lacy Cu-S product are predominant crystal forms in upper layer. Calcium carbonate can be found in packets, surrounded by nodules of Fe. Carbonate is in elongate pseudo-hexagonal crystals.
14	Thick, brown, adherent microcrystalline coating	Coating is predominantly carbonate crystals, covered with Fe nodules. Coating also contains lacy crystals whose edx peaks show copper and sulfur.
20	Thin, adherent, tarnished, brown product with patches of blue and green	Thin product with swiss cheese appearance, composed of Cu and Cl.
22	Thick, adherent, black coating	Coating is predominantly rounded nodules of Cu and S doped with Ni and Al. Coating contains less than 3% pseudo-hexagonal crystals with edx analysis showing peaks of Cu and S.
24	Thick, non-adherent dark gray coating	Upper layer is predominantly tabular pseudo-hexagonal crystals with edx analysis showing peaks of Cu and S.
26	Thick, non-adherent black coating	Upper layer is predominantly packets of acicular carbonate crystals. The layer underneath carbonate is predominantly tabular pseudo-hexagonal crystals. Layer also contains lacy products rich in Cu and S. Nodules of Cu-S-Ni-Fe are intermixed with pseudo-hexagonal tabular crystals.
30	Thick, brownish gray adherent product	Upper layer predominantly, pseudo-hexagonal tabular crystals. Lacy crystals rich in Cu and S are also abundant. Porous surface layer of Cu and S doped with Ni.
32	Thick, crystalline, brown, adherent product, with green and yellow corrosion product at edges	Surface is abundantly coated by lacy crystals with edx analysis of Cu and S. Pseudo-hexagonal crystals of Cu-S, made up less than 5% of total corrosion product. Botryoidal crystals of Cu were abundant beneath acicular crystals.
34	Thick, black, adherent coating, covered with white acicular crystals	Coating is predominantly pseudo-hexagonal crystals rich in Cu and S. Less abundant are carbonate crystals, and Cu-S lacy plates and nodules.
36	Thick, brown, adherent coating	Coating is predominantly tabular, pseudo-hexagonal crystals of Cu-S. Carbonate crystals were intermixed with pseudo-hexagonal crystals. Nodules of Cu with S, Ca, Fe, Al covered some of the pseudo-hexagonal crystals.

Table 3: Possible identification of corrosion products by crystal form and edx analysis.

Specimen Number	aragonite	Cuprite Cu_2O	chalcocite Cu_2S	covellite CuS	atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$	unidentified mineral constituents
2		surface layer				
4	top layer	surface layer			top layer	
6	rare, top layer		?	?		Nodules, containing predominantly Cu and S, doped with Ni, Fe, and Al.
8		surface layer	?	?		Nodules, containing predominantly Cu and S, doped with Ni, Fe, and Al. Rounded nodules composed predominantly of Ni.
16		surface layer	top layer			
10		surface layer		?		Lacy crystals with saw blade edges, with edx analysis of Cu and S were not identified.
12			predominate in top layer	?		Lacy crystals with saw blade edges, constituents are Cu and S. Carboante crystals are surrounded by Fe rich nodules.
14	predominate in top layer					Carbonate crystals are surrounded by Fe rich nodules. Lacy crystals with edx analysis of Cu and S are less abundant than carbonate crystals.
20					predominate in coating	
22			rare top layer	?		Coating is predominantly nodules of Cu and S doped with Ni and Al.
24			predominate in top layer			
26	predominate in top layer		layer beneath carbonate	?		Lacy crystals with saw blade edges, predominate constituents are Cu and S. Nodules rich in Cu, S, Ni, Fe were intermixed in chalcocite layer.
30			predominate in top layer	?		Surface layer appears to be porous, composed of Cu and S. Lacy crystals with saw blade edges, with Cu and S as primary constituents were abundant in chalcocite rich layer.
32			rare, top layer	?		Lacy crystals with saw blade edges, with Cu and S as primary constituents.
34	rare, top layer		predominate in top layer	?		Lacy crystals with saw blade edges, composed of Cu and S. Nodules rich in Cu and S.
36	top layer		predominate in top layer			Nodules rich in Cu, Fe, Al, S covered carboante crystals and chalcocite crystals.

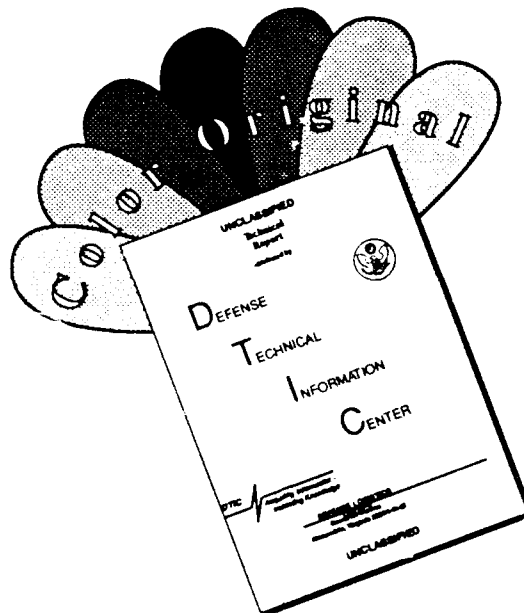
Table 4
Sample Data in aerated solutions

Sample Number	weight begin (grams)	weight end (grams)	precipitate weight (grams)	corrosion time (days)	solution
1	2.2950	2.4814	0.1864	139	1-A
2	2.0010	2.0759	0.0749	139	1-A
3	2.3640	2.4793	0.1153	139	2-A
4	2.3585	2.4934	0.1349	139	2-A
5	2.2525	2.4156	0.1631	139	3-A
6	2.7315	2.8203	0.0888	139	3-A
7	2.5822	2.6670	0.0848	139	4-A
8	2.2845	2.4084	0.1239	139	4-A
16	2.3967	2.4862	0.0895	122	5-A
17	2.2175	2.3267	0.1092	122	5-A
10	2.2359	2.4043	0.1684	122	6-A
11	2.2817	2.4390	0.1573	122	6-A
12	2.5205	2.5366	0.0161	122	7-A
13	2.4172	2.4360	0.0188	122	7-A
14	1.9882	2.0000	0.0118	122	8-A
15	2.2970	2.3125	0.0155	122	8-A

Table 5
Sample data in Deaerated Solutions

Sample Number	Weight begin grams	Weight end grams	Precipitate weight grams	Corrosion time days	Solution
20	2.2155	2.3506	0.1351	120	1-D
21	2.2292	2.3668	0.1376	120	1-D
22	2.4475	2.6237	0.1762	120	2-D
23	2.2265	2.3857	0.1592	120	2-D
24	2.2137	2.4062	0.1924	120	3-D
25	2.2175	2.3926	0.1751	120	3-D
26	2.3466	2.5285	0.1819	120	4-D
27	2.2312	2.4090	0.1778	120	4-D
30	2.2150	2.2198	0.0048	119	5-D
31	2.4994	2.6145	0.1151	119	5-D
32	2.2017	2.3661	0.1644	119	6-D
33	2.2289	2.3820	0.1531	119	6-D
34	2.4984	2.6740	0.1756	119	7-D
35	2.4577	2.6267	0.1690	119	7-D
36	2.2084	2.3934	0.1837	119	8-D
37	2.1588	2.3216	0.1628	119	8-D

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